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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

CONCERNING POSITION ISOMERISM AND HEATS OF COMBUSTION.

By Lawrence J. Henderson.

Presented by T. W. Richards, January 9, 1907. Received December 20, 1906.

Current ideas of valence consist of two distinct conceptions, quantivalence and valence energy, which rest upon two bodies of fact of different sorts. Of these conceptions quantivalence has played by far the greater rôle in the development of organic chemistry and of stereochemistry, though the consideration of valence energy is present or implied in Le Bel's discussion of the asymmetric carbon atom, in von Baeyer's "Spannungstheorie," in Thiele's theory of partial valence, and in Werner's stereochemical theories and recent publications. In Richards's recent discussions of the compressible atom the conception of valence energy has shown itself more pertinent than the conception of quantivalence, and in the theoretical discussion of thermochemical data it has been, and of course is, of the greatest moment.

Conclusions regarding valence energy which are based upon heats of combustion are open to the criticism that from measures of the magnitude of the total-energy change it is sought to determine the magnitude of a quantity which depends perhaps entirely upon the free-energy change. Yet even to-day the determination of heats of combustion remains the one way possible of gaining quantitative data regarding the magnitude of valence energy in organic compounds, and it is probable that such information, properly interpreted, leads to not inaccurate conclusions. On the contrary, these conclusions may be very accurate when differences between the heats of combustion of similar substances are considered, and when such differences in very similar cases are compared, as in this paper, there is good reason to believe that changes in bound energy have been almost wholly eliminated.

Of these two ideas concerning valence, that of valence energy is the less clearly defined. J. Thomsen, it is true, has sought to show that the energy involved in producing a union between any two atoms is the same for all cases of that particular union, excluding double and treble ties, but without regard to the constitution of the rest of the molecule, and with the aid of this theory he has woven the fabric of his complicated thermochemical hypotheses. But, as I have shown in another place,[1] unless together with valence energy other considerable energy relationships exist within the molecule, a possibility as yet unsupported by fact, the energy of the tie between two atoms is variable, and dependent upon the nature of every other atom of the molecule and its position. This logical deduction was established by the consideration of such processes as the substitution of hydrogen by hydroxyl to form primary alcohols or acids as the case may be. The average values of the change in heat of formation of the molecules in these two cases are

$$\mathrm{R\,CH_3 - R\,CH_2\,OH = 40\ Cal.}$$
$$\mathrm{R\,CHO - R\,COOH = 72\ Cal.}$$

If we assume that the valence energy of a tie between two atoms is constant for all cases of the union, and exclude the possibility of other considerable energy relationships within the molecule, it is clear that these two values, 40 Cal. and 72 Cal., should be identical. Therefore the assumption is incorrect.

This conception of varying valence energy is, indeed, old. It was originally stated without experimental basis by Claus,[2] and, again as a theory, was developed by Werner[3] in his original discussion of his stereochemical ideas. More recently[4] the significance of comparative reactions has been carefully considered in this connection, and from that point of view much evidence has been adduced in support of the idea of variable valence energy.

The influence of the nature of those atoms of a molecule which are not directly concerned in a reaction of the molecule upon the heat of a reaction, an influence which must manifest itself in part through variations in the dependent valence energies of the reacting atoms, I have already briefly discussed;[5] with existing data little more can be said, and I postpone the discussion of this aspect of the question till the necessary experimental data are at hand, investigations to this end being now in progress in this laboratory.

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[1] Journal of Physical Chemistry, **9**, 40-56 (1905).

[2] Berichte **14**, 432 (1881).

[3] Vierteljahrsschrift d. Züricher Naturforscher Gesellschaft (1891).

[4] Werner, Berichte, **39**, 1278 (1906). Flürscheim, Jour. f. prakt. Chem., **66**, 321 (1902); **71**, 497 (1905); Berichte, **39**, 497 (1905).

[5] l. c.

On the other hand, the influence of the relative positions of its atoms upon the heat of reaction of a molecule, and consequently upon the valence energies of the reacting atom, is an interesting subject which in some of its aspects may be discussed with the aid of existing data.

The following tables contain the available data which show that the introduction of a foreign group into a molecule influences the heat of a reaction of an atom group of that molecule in a varying degree according to the relative positions of the two groups.

I.

$CH \longrightarrow C\text{–}CH_3$

A

COOH present.[6]

			Cal.
α	$CH_3 \cdot COOH - H \cdot COOH$	207 − 59	= 148
β	$C_2H_5 \cdot COOH - CH_3 \cdot COOH$	364.0 − 206.7	= 157.3
higher	$C_2H_5 \cdot C_nH_{2n} \cdot COOH - CH_3 \cdot C_nH_{2n} \cdot COOH$		= 156.5

B

$CONH_2$ present.[7]

α	$CH_3 \cdot CONH_2 - H \cdot CONH_2$	283 − 135	= 148
β	$C_2H_5 \cdot CONH_2 - CH_3 \cdot CONH_2$	439.8 − 282.7	= 157.1
higher	$C_2H_5 \cdot C_nH_{2n} \cdot CONH_2 - CH_3 \cdot C_nH_{2n} \cdot CONH_2$		= 156.1

C

$CONHC_6H_5$ present.[7]

α	$CH_3 \cdot CONH\,C_6H_5 - H \cdot CONH\,C_6H_5$	1011 − 861	= 150
β	$C_2H_5 \cdot CONH\,C_6H_5 - CH_3 \cdot CONH\,C_6H_5$	1168 − 1011	= 157
higher	$C_2H_5 \cdot C_nH_{2n} \cdot CONH\,C_6H_5 - CH_3 \cdot C_nH_{2n} \cdot CONH\,C_6H_5$		= 156.2

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[6] Stohmann, Jour. f. prakt. Chem., **49**, 107 (1894).

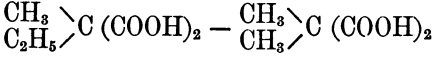
[7] Id., **52**, 59 (1895).

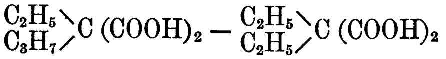
D

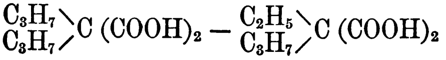
$CH(COOH)_2$ present.[8]

α $CH_3 \cdot CH(COOH)_2 - H \cdot CH\,(COOH)_2$ $362 - 207 = 155$

α $(CH_3)_2\,C\,(COOH)_2 - CH_3 \cdot CH\,(COOH)_2$ $515 - 362 = 153$

β 
$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > C\,(COOH)_2 - \begin{matrix} CH_3 \\ CH_3 \end{matrix} > C\,(COOH)_2$ $676 - 515 = 461$

γ 
$\begin{matrix} C_2H_5 \\ C_3H_7 \end{matrix} > C\,(COOH)_2 - \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > C\,(COOH)_2$ $990 - 833 = 157$

γ 
$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix} > C\,(COOH)_2 - \begin{matrix} C_2H_5 \\ C_3H_7 \end{matrix} > C\,(COOH)_2$ $1146 - 990 = 156$

E

CO present.[9]

α $CH_3 \cdot CO \cdot CH_3 - CH_3 \cdot CHO$ $437 - 282 = 155$

α $C_3H_7 \cdot CO \cdot CH_3 - C_3H_7 \cdot CHO$ $754 - 600 = 154$

β $CH_3 \cdot CH_2 \cdot CHO - CH_3 \cdot CHO$ $441 - 282 = 159$

β $(CH_3)_2 \cdot CH \cdot CHO - CH_3 \cdot CH_2 \cdot CHO$ $600 - 441 = 159$

F

COH present.[10]

α $CH_3 \cdot CH_2OH - CH_3OH$ $326 - 171 = 155$

α $CH_3 \cdot CHOH \cdot CH_3$[11] $- CH_3 \cdot CH_2OH$ $478 - 322 = 156$

α $(CH_3)_3\,COH - (CH_3)_2\,CHOH$ $633 - 478 = 155$

β $C_2H_5 \cdot CH_2OH - CH_3 \cdot CH_2OH$ $480 - 322 = 158$

β $(CH_3)_2\,CH \cdot CH_2OH - CH_3 \cdot CH_2 \cdot CH_2OH$ $637 - 480 = 157$

β $(CH_3)_2\,C_2H_5 \cdot COH - (CH_3)_3\,COH$ $788 - 633 = 155$

Averages.

$$C_nH_{2n+1}CH_3 - C_nH_{2n+1}H = 156.2 \text{ Cal.}$$

In the Presence of	α	β	γ	higher.
COOH	148	157.3	156–157	156.5
$CONH_2$	148	157.1	156–157	156.1
$CONH\,C_6H_5$	150	157.0	156–157	156.2
$CH\,(COOH)_2$	154	161	156–157	. . .
CO	154.5	159	. . .	. . .
COH	155.3	156	. . .	. . .

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[8] Id., pp. 114, 116. [9] Thomsen, Thermochemische Untersuchungen.

[10] See Stohmann's tables, Zeits. f. physikal. Chem., **6**, 334 (1890); **10**, 410 (1892).

[11] Louguinine's values are here changed; see Henderson, Jour. of Physical Chemistry, **19**, 43 (1905).

Differences from 156.2 *Cal., the "normal" Value.*

In the Presence of	α	β	γ	higher.
COOH	–8	+1	0	0
$CONH_2$	–8	+1	0	0
$CONH\,C_6H_5$	–6	+1	0	0
$CH \cdot (COOH)_2$	–2	+5	0	. . .
CO	–2	+3	. . .	. . .
COH	–1	0	. . .	. . .

II.

$CH_3 \longrightarrow COOH$

A

COOH present.[12]

α	$CH_3 \cdot COOH - COOH \cdot COOH$	207 – 60 = 147
β	$CH_3 \cdot CH_2 \cdot COOH - COOH \cdot CH_2 \cdot COOH$	364 – 207 = 157
γ	$CH_3 \cdot (CH_2)_2 \cdot COOH - COOH \cdot (CH_2)_2 \cdot COOH$	520 – 357 = 163
δ	$CH_3 \cdot (CH_2)_3 \cdot COOH - COOH \cdot (CH_2)_3 \cdot COOH$	677 – 515 = 162
ε	$CH_3 \cdot (CH_2)_4 \cdot COOH - COOH \cdot (CH_2)_4 \cdot COOH$	832 – 669 = 163
ζ	$CH_3 \cdot (CH_2)_5 \cdot COOH - COOH \cdot (CH_2)_5 \cdot COOH$	989 – 829 = 160
η	$CH_3 \cdot (CH_2)_6 \cdot COOH - COOH \cdot (CH_2)_6 \cdot COOH$	1145 – 984 = 161
θ	$CH_3 \cdot (CH_2)_7 \cdot COOH - COOH \cdot (CH_2)_7 \cdot COOH$	1302 – 1141 = 161
ι	$CH_3 \cdot (CH_2)_8 \cdot COOH - COOH \cdot (CH_2)_8 \cdot COOH$	1458 – 1297 = 161

β	$CH_3 \cdot CH_2 \cdot COOH - COOH \cdot CH_2 \cdot COOH$	364 – 207 = 157
β	$CH_3 \cdot (CH_2)_2 \cdot COOH - CH_3 \cdot CH\,(COOH)_2$	520 – 362 = 158
β	$CH_3 \cdot (CH_2)_3 \cdot COOH - C_2H_5 \cdot CH\,(COOH)_2$	677 – 518 = 159
β	$CH_3 \cdot (CH_2)_3 \cdot COOH - (CH_3)_2 \cdot C\,(COOH)_2$	677 – 515 = 162
β	$CH_3 \cdot (CH_2)_4 \cdot COOH - \genfrac{}{}{0pt}{}{CH_3}{C_2H_5} \!\! > C\,(COOH)_2$	832 – 676 = 156
β	$CH_3 \cdot (CH_2)_4 \cdot COOH - C_3H_7 \cdot CH\,(COOH)_2$	832 – 675 = 157
β	$CH_3 \cdot (CH_2)_5 \cdot COOH - (C_2H_5)_2 \cdot C\,(COOH)_2$	989 – 833 = 156
β	$CH_3 \cdot (CH_2)_6 \cdot COOH - \genfrac{}{}{0pt}{}{C_2H_5}{C_3H_7} \!\! > C\,(COOH)_2$	1145 – 990 = 155
β	$CH_3 \cdot (CH_2)_7 \cdot COOH - (C_3H_7)_2 \cdot C\,(COOH)_2$	1302 – 1146 = 156
β	$CH_3 \cdot (CH_2)_8 \cdot COOH - C_7H_{15} \cdot CH\,(COOH)_2$	1458 – 1303 = 155
β	$CH_3 \cdot (CH_2)_9 \cdot COOH - C_8H_{17} \cdot CH\,(COOH)_2$	1616 – 1458 = 158

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[12] Stohmann, Jour. f. prakt. Chem., **49**, 107, 114, 116 (1894).

Averages.

$$C_nH_{2n+1}CH_3 - C_nH_{2n+1}COOH = 160 \text{ Cal.}$$

	α	β	γ, δ, ε	higher.
In the presence of COOH	147	157	163	161

Differences from 160 *Cal., the "normal" Value.*

	α	β	γ, δ, ε	higher.
In the presence of COOH	−13	−3	+3	+1

III.

$CH_3 \longrightarrow CONH_2$[13]

A

CONH$_2$ present.

α $CH_3 \cdot CONH_2 - CONH_2 \cdot CONH_2$ $283 - 203 = 80$

β $CH_3 \cdot CH_2 \cdot CONH_2 - CONH_2 \cdot CH_2 \cdot CONH_2$ $440 - 359 = 81$

γ $CH_3 \cdot CH_2 \cdot CH_2 \cdot CONH_2 - CONH_2 \cdot CH_2 \cdot CH_2 \cdot CONH_2$ $596 - 510 = 86$

Summary.

$$C_nH_{2n+1}CH_3 - C_nH_{2n+1} \cdot CONH_2 = 83 \text{ Cal.}$$

	α	β	γ
In the presence of CONH$_2$	80	81	86

Differences from 83 *Cal., the "normal" Value.*

	α	β	γ
In the presence of CONH$_2$	−3	−2	+3

IV.

$CH_3 - CONH\,C_6H_5$[14]

A

COOH present.

α $CH_3 \cdot COOH - C_6H_5 \cdot NH \cdot CO \cdot COOH$ $207 - 863 = -656$

β $CH_3 \cdot CH_2 \cdot COOH - C_6H_5 \cdot NH \cdot CO \cdot CH_2 \cdot COOH$ $364 - 1013 = -649$

γ $CH_3 \cdot (CH_2)_2 \cdot COOH - C_6H_5 \cdot NH \cdot CO \cdot (CH_2)_2 \cdot COOH$ $520 - 1166 = -646$

Summary.

$$C_nH_{2n+1}CH_3 - C_nH_{2n+1}CONH\,C_6H_5 = -645 \text{ Cal.}$$

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[13] Id., **52,** 59 (1895); **55,** 263 (1897).

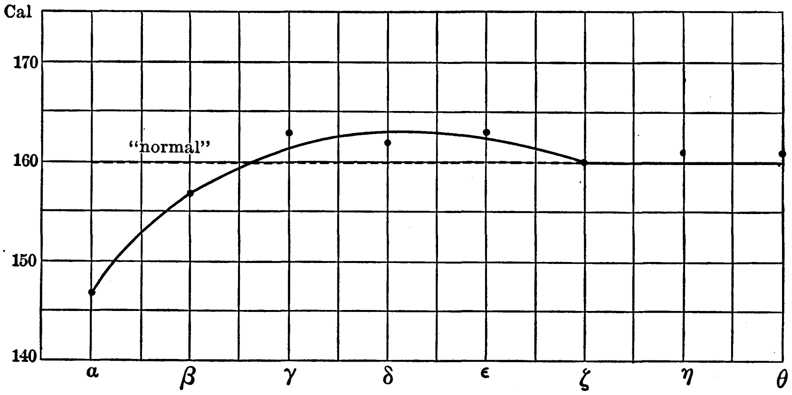
[14] Id.

	α	β	γ
In the presence of COOH	—656	—649	—646

Differences from —645 Cal., the "normal" Value

	α	β	γ
In the presence of COOH	—11	—4	—1

It is apparent from a consideration of the above tables that the effect upon the heat of reaction of a molecule exerted by a group which is itself not directly concerned in the reaction varies in a regular way with variation in the position of the group with respect to the reacting portion of the molecule. This is most clearly apparent in the reaction CH_3 — COOH in the presence of the group COOH, probably because here the effect is great and the data abundant and accurate. In this case, when the carboxyl group is α to the reacting group the heat of reaction is diminished by 13 Cal., compared with its "normal" value in the absence of the carboxyl group; when the carboxyl group is in the β position the heat of reaction is diminished by about 3 Cal.; when the carboxyl group is in the γ, δ or ε position it is increased by about 2.5 Cal., returning finally to the "normal" value when the distance between the two groups is greater. The effect may be represented by the accompanying curve.[15]



Curve I.

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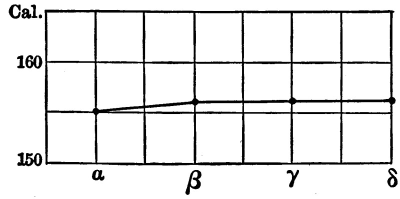
[15] The nature of this curve is apparently inconsistent with the idea developed by Flürscheim (l. c.) and by Biach (Zeits. f. physikalische Chemie, **50**, 43, 1904) that valence energy alternately increases and decreases from one carbon atom to the next, in a chain or ring; the period of alternation being, in the present matter, sometimes one carbon atom, sometimes more, according to the nature of the case.

It is clear in all the above cases that the effect of a group upon the heat of reaction is greatest when it occupies the α position, and that when it is sufficiently distant from the reacting group, this necessary distance varying with the nature of the case, it has no appreciable effect. Evidently, too, in most cases, before the effect disappears it is reversed, as in the γ, δ, and ε positions on the above curve and in the β position in those cases where the effects of the groups COOH, $CONH_2$, etc., upon the reaction $CH - C\,CH_3$ are considered.

In most cases an atom or atom group does not appreciably influence the heat of a reaction when the reacting group is further away from it than the β or γ position, and it may be noticeable only when it occupies the α position, as in the case represented by the accompanying curve.



Curve II.

In the case represented by the first curve, however, an effect is still notable when the two groups are in the ε position to each other, provided the data are nearly correct, and it is important to consider that the data for this series of compounds are perhaps the best of all Stohmann's admirable determinations. Accordingly it is not impossible that curve I represents at least one general case of variation in heat of reaction with variation in position of an inactive group; at any rate the data here represented is not inconsistent with such a conclusion, and for the most part the curves would be of similar shape.

These regularities in the variation of heats of reaction which have been here considered, as well as those previously pointed out, lead naturally to the conclusion that the valence energy of a tie between two atoms must be capable of *continuous variation*[16] within certain limits, not yet to be defined; otherwise we must assume the existence of large forces of unknown nature within the molecule. *According to this conclusion and the above considerations the valence energies of two ties between like atoms will under like conditions be equal, under unlike conditions different.* Thus in the compound CR_4

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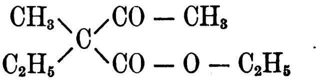
[16] Or, what is less probable, through numerous distinct magnitudes discontinuously.

the four valence energies of the central carbon atom will be equal, in the compound $CR'R''_3$ three will be equal and one different from these three; and in the compound $CR'R''R'''R''''$ all four will be different, even when the central carbon atom is tied to like atoms by all four of its valences as in methylethylacetacetic ester



$$\begin{array}{c} CH_3\diagdown \quad \diagup CO - CH_3 \\ C \\ C_2H_5\diagup \quad \diagdown CO - O - C_2H_5 \end{array}$$

because every one of the four carbon atoms which are tied to the central carbon atom is different in position from every other and consequently subjected to different influences from at least some of the atoms of the molecule.

It cannot be too strongly emphasized that this conclusion is a logical deduction from established experimental data with the aid of but two postulates, the current theory of chemical constitution and the current theory that the interatomic forces within the molecule are exclusively (or almost exclusively) valence energies.

It remains to be pointed out that through the consideration of many cases similar to those here studied, one may hope to obtain accurate quantitative information regarding the phenomena of orientation of substituting groups[17] and the countless other cases familiar to every organic chemist of the influencing of reaction by substituted groups, and thus to replace the existing empirical rules for such cases by accurately formulated principles.

SUMMARY.

In development of the conception of varying valence energy it is shown that the effect of an inactive atom group upon a reaction of another atom group of the same molecule, measured by the heat of reaction, varies in a regular way according to the relative positions of the two groups.

Curves are presented representing the nature of this variation in one case of special importance because of the magnitude of the effect and the accuracy of the data, and in a case where the effect is slight.

It is shown that, in accordance with this conclusion and the previous considerations, the valence energies of two ties between like atoms are under like conditions equal, under unlike conditions different.

The importance of these considerations for the understanding of the influencing of reactions by substituted groups is pointed out.

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[17] See for instance Flurscheim, l. c.